Capacitance and Series Resistance determination in high power ultracapacitors

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The ultracapacitor measurement methodology is an open topic. Recently an addition to standard IEC 62391 has been submitted to the IEC organization to propose measurement methods for characterizing ultracapacitors. The basic difficulty is related to the capacitance and series resistance increase with the applied voltage.

A recent paper[1] has shown that the capacitance is mainly driven by the space charge within the electronic conductor. The capacitance is indeed composed of a series connection, one due to the space charge layer inside the conductor and the second to the Helmoltz layer in the electrolyte.

The capacitance is basically defined by the relation:

$$C_u = \frac{Q(U_c)}{U_c},$$

where $Q(U_c)$ is the accumulated charge on the electrode at the voltage U_c, which in our case varies with the voltage applied at the capacitor terminals.

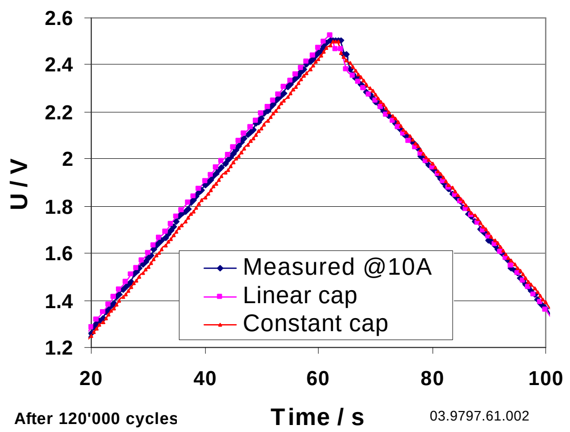

Figure 1: Convex 10 A charging curve for the BOOSTCAP® type BCAP0350 with a nominal capacitance of 350F and a series resistance of 2.4 mO, measured after 120'000 cycles.

The capacitance can be described as the sum of a constant and a voltage dependent term,

$$C_u = C_o + K \cdot U_c,$$

where C_0 is the capacitance at 0 V. The current in the dc-limit is given by the classical relation $i = \frac{dQ}{dt}$. Taking into account the time dependency of the capacitance, it becomes

$$i(t) = (C_o + 2 \cdot K \cdot |U_c|)\frac{dU_c}{dt}.$$

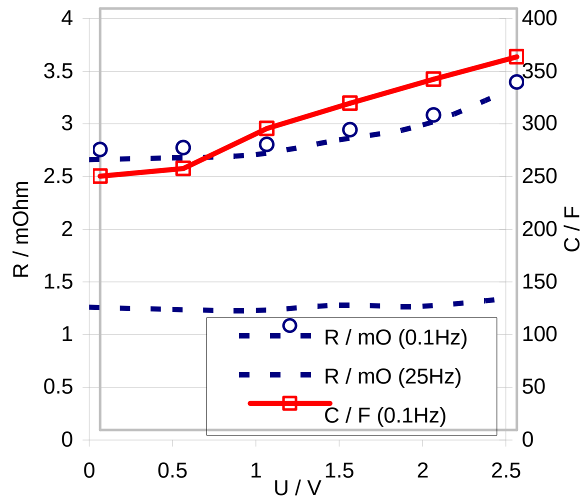

Figure 2: Resistance R_s (at 0.1 Hz and 25 Hz) and capacitance C_{iu} (at 0.1 Hz) versus voltage of BCAP0350.

The voltage dependant capacitance value, C_{iu}, in Figure 2 is defined by,

$$C_{iu} = C_o + 2 \cdot K \cdot |U_c|,$$

and the nominal capacitance, C_n, is defined as the mean C_{iu} value between the nominal voltage U_n and $U_n/2$:

$$C_n = C_o + \frac{3}{2} \cdot K \cdot |U_n|.$$

This relation states, that for a given voltage variation, higher currents are available in the higher voltage range.

Thus, in order to characterize the Boostcap capacitance at low frequency, it is necessary to give at least two parameters C_o and K. In the case of a 120'000 cycles aged BCAP0350, C_o = 250 [F] and K = 25 [F/V]. Figure 3 shows the SIMPLORER based electronic circuit description of the above model. It is to note that at 2.5 V the capacitance C_{iu} is 40% bigger than at 0V.

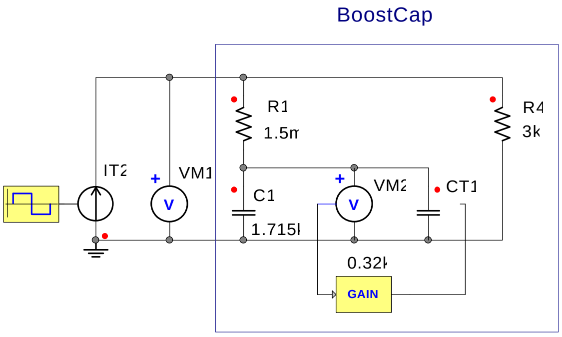

Figure 3: Linear capacitance model

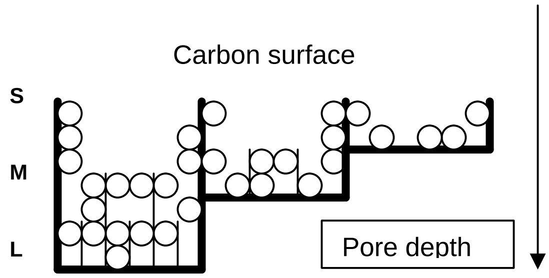

Figure 5: Pore-model

Frequency & voltage model

From this starting point we have developed a more general Frequency Voltage Model. The electrical scheme is shown in figure 4. It takes into account the voltage and the frequency dependencies of both the capacitance and the series resistance.

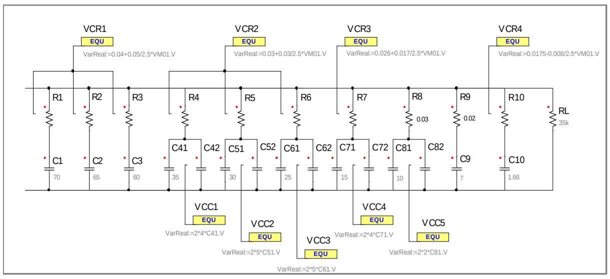

Figure 4: Frequency voltage model

This new model for dynamic analysis consists of ten layers. The necessary parameters are determined by 2 couples (for 0 V and 2.5 V) of distributions for the series resistance and the capacitance shown in figure 6 and 7. Each distribution is defined for 10 different types of surface contributing to the capacitance. Surface “10” corresponds to the layer near the carbon surface. Surface “1” corresponds to the deepest surface in the activated carbon. This latter surface type collects the highest part of the capacitance, but is difficult to reach for the ions. The model put together the well-known transmission-line model of de Levie[2] and the parallel-RC model of Zubieta.[3] Related models have been used by Dougal[4] and Belhachemi [5,6].

Figure 5 depicts the geometric pore structure the Frequency Voltage model is based on. Accordingly, the porous electrodes have three different stages of accessibility, being characterized by a Weibull distribution of capacitance and resistance.

The easiest accessible capacitance lies close to the pore surface.

Most of the surface lies deep in the pores. To reach this surface the ions have a longer way. Consequently the series resistance increases due to the more difficult access for the ions. This does mean that this surface is only accessible in the low frequency domain.

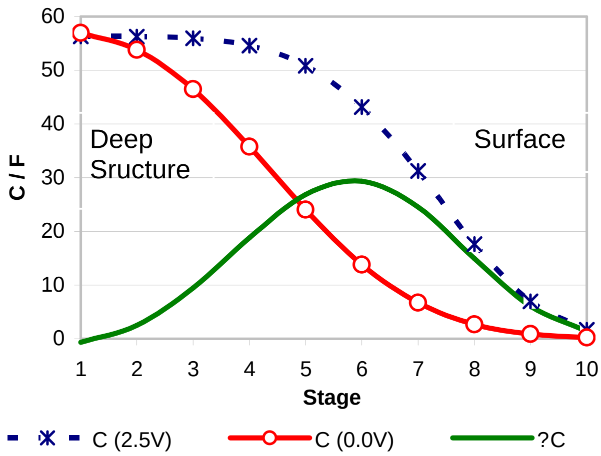

Figure 6 : Capacitance distribution at 0 and 2.5 V

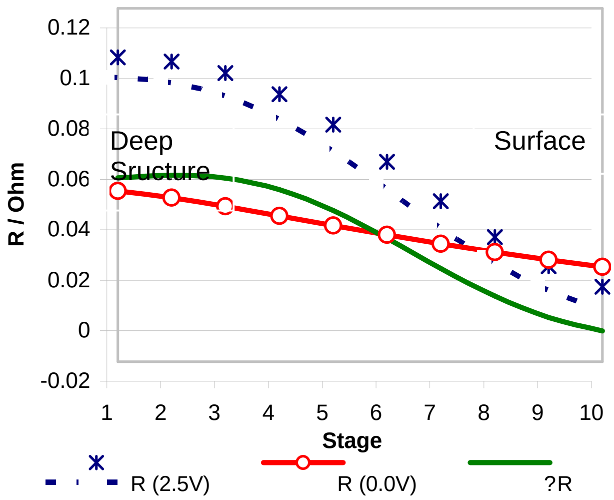

Figure 7: Resistance distribution at 0 and 2.5 V

Results

The correlation of the Voltage Frequency Model with experimental measurements has been verified by impedance spectroscopy between 0.1 and 1000 Herz. The results are displayed in figure 8 and 9 for the impedance spectrometry.
The capacitance drop shape with the frequency depends on the electrode carbon type. A good technology is characterized by a capacitance drop as high as possible frequency.

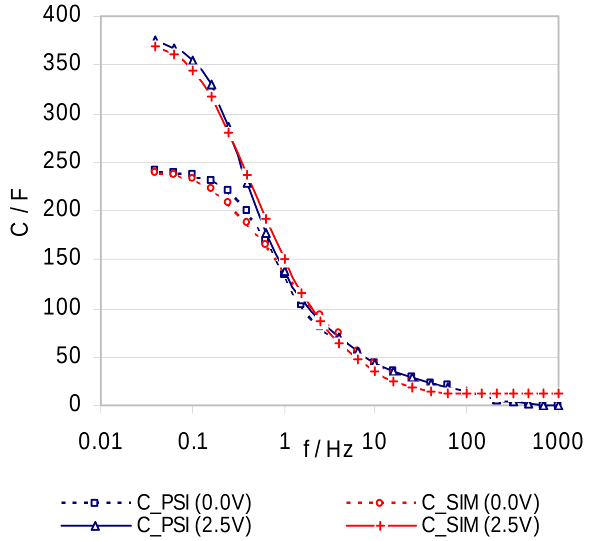

Figure 8 : Comparison of capacitance from frequency (impedance) spectrum

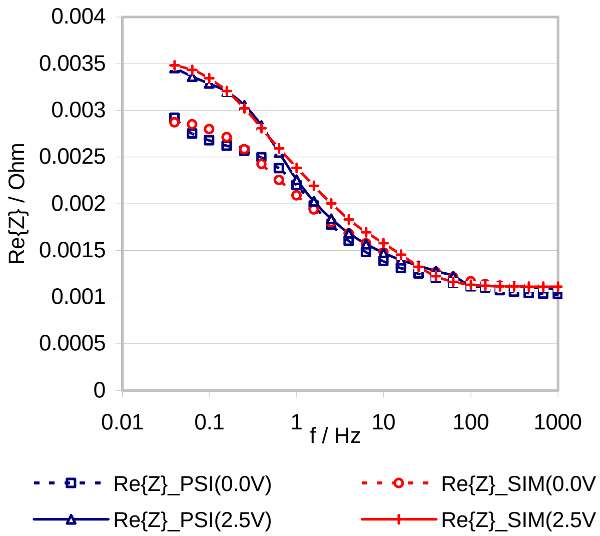

Figure 9: Comparison of resistance from frequency (impedance) spectrum

From the impedance spectra, it is obvious that at high frequency the capacitance value C_{iu} doesn't change with the voltage. In other words the surface accessibility depends on the voltage only for the deep structure.

The correlation of the Voltage Frequency Model has been also verified in the time domain. Figure 1 compares the experimental charging curve of a BCAP0350A01 with a 10A constant current, with the result of the Simplorer simulation using the model parameters.

Figure 10 shows the BCAP0350A01 frequency voltage dependency for an operating voltage of 1.25V and a current load of 20 A.

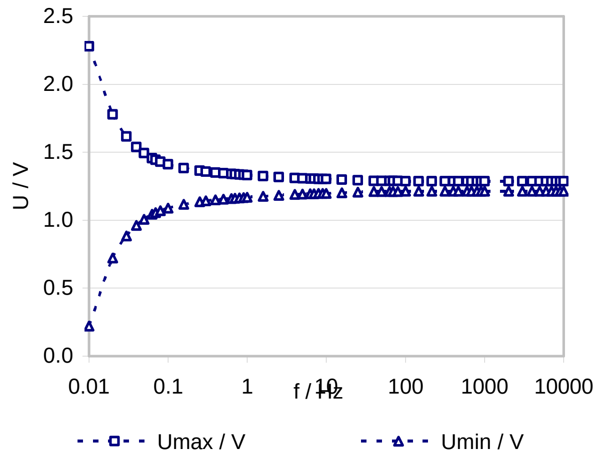

Figure 10: Voltage cover curves for AC-load versus frequency

Voltage cover curves shows max. and min. voltage for discrete frequencies. For constant charge and discharge time (equal a constant frequency) the voltage alternates between one point of the upper and one point of the lower curve. The curves are calculated for an ideal current start phase angel of 0°. For other start phase angel a transient part must be considered.

The model could be extended to take into account the temperature dependence of the ultracapacitor properties. Some measurements on BCAP0010 are available in the literature[7].

Maxwell Technologies intends to supply for each of its ultracapacitor types the required simulation parameters. The power electronic engineers can use these parameters to model their applications.

Acknowledgement

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